

Many-Dimensional Quantum Energy Flow at Low Energy

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Criteria for ergodicity and rates of energy flow in a quantum mechanical system of N coupled anharmonic oscillators where N is large are determined at energies near the ground state of the system. High-order resonances are important for the transition at large N . The role of numerous virtual transitions, "vibrational superexchange," in global transport is examined both for typical parts of the state space and special states often interrogated experimentally.

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Understanding the origin and nature of irreversibility in finite quantum systems is an ongoing pursuit. The path toward establishing criteria for ergodicity in quantum systems of low dimension has been guided by the correspondence principle limit of classical dynamics [1–3]. Because of their inherently large state space, however, many-dimensional quantum systems may be usefully described by statistical concepts such as ergodicity even at low excitation. Still, much less is known about the nature of quantum energy flow in many-dimensional systems [3–6]. Quantum ergodicity and the rate of equilibration play, moreover, a central role in dynamical theories of finite many-body systems such as nuclei, molecules, and clusters. Insight into the nature of quantum energy flow can be drawn from the numerous studies in few dimensions, such as the relationship to classical chaos and the possibility of its quantum mechanical suppression. Much attention has focused on driven systems [7] and two coupled anharmonic oscillators [8], where finite \hbar corrections to the semiclassical limit localize the quantum system to only part of its energetically allowed space while the corresponding classical system can roam freely throughout it. The nature of quantum irreversibility in many-oscillator systems is less well understood, but there are strong indications that quantum suppression of chaos also occurs when N is large. Logan and Wolynes (LW) [4] have put forward arguments suggesting high dimensional systems of nonlinearly coupled oscillators undergo a localization transition akin to the Anderson transition [9] of single particle transport in disordered systems. In many-dimensional systems quantum effects may also permit flows prohibited by classical mechanics. Heller and Davis [10] conjectured that in large molecules, enabled by a high density of states, vibrational relaxation could occur among all energetically available modes via a classically forbidden mechanism they called "dynamical tunneling," that allows transitions among invariant tori to which classical motion would be otherwise confined. In quantum systems of high dimension, not only \hbar but also N serves as a parameter tuning the transition to ergodicity. Seeking to address the interplay between dynamical tunneling and localization, in this Letter we explore the origins and extent of quantum irreversibility at low energy, in a system that mimics in some respects large

molecules or clusters. We find criteria for ergodicity and rates of energy flow among N coupled anharmonic oscillators, where N is large, at energies near the ground state of the system, i.e., much below that at which a typical oscillator has even a single quantum of excitation. The model contains very high-order nonlinear resonant processes that play a crucial role. At low total energy, energy flow can involve numerous virtual transitions in state space; in some sectors a large number are needed to bridge two resonant states. This process, called "vibrational superexchange," has been the subject of recent investigations [11,12] scrutinizing vibrational energy transfer in specific molecules such as *t*-butylacetylene and 1-propyne. The role of vibrational superexchange towards energy flow in our model, and the contribution of high-order resonances to a transition to global flow at low energies is elucidated below.

We study a system of N oscillators with total excitation reaching no more than $m = N^\gamma$ quanta, $0 < \gamma < 1$, so that the system lies near its ground state. The Hamiltonian is $H = H_0 + V$, where

$$H_0 = \sum_{\alpha=1}^N \epsilon_{\alpha}(\hat{n}_{\alpha}), \quad (1a)$$

$$V = \sum_{\mathbf{m}} \prod_{\alpha} \phi_{\mathbf{m}} b_{\alpha_i}^{\dagger m_i^+} b_{\alpha_i}^{m_i^-}, \quad (1b)$$

$\alpha = \{\alpha_1, \alpha_2, \dots\}$ and $\mathbf{m} = \{m_1^{\pm}, m_2^{\pm}, \dots\}$. H contains not only the familiar low-order Fermi resonances but also higher-order direct resonances that we assume satisfy a scaling relation [12], $\phi_{\mathbf{m}} = (-1)^p \phi_3 \sigma^{3-p}$ ($p \geq 3$), where $p = \sum_{i=1}^p (m_i^+ + m_i^-)$. Each p -tuple of coupling terms in (1b) is taken from a set of $Z^p = N^{\delta p}$, $0 \leq \delta \leq 1$, oscillators to which a given oscillator can directly couple. When $\delta = 1$ each oscillator couples directly to all others, while for $\delta < 1$ H is sparse, thereby introducing additional locality to excitation transfer; the effective local density of states, $\rho_l(E)$, to which a zero-order state of H couples is much smaller than the global level density, $\rho_g(E)$, for large N when $\delta < 1$. The number operator is defined by $\hat{n}_{\alpha} = b_{\alpha}^{\dagger} b_{\alpha}$, and oscillators of H_0 have frequency $\omega_{\alpha}(n_{\alpha}) = \hbar^{-1} \partial \epsilon_{\alpha}(n_{\alpha}) / \partial n_{\alpha}$ and nonlinearity $\omega'_{\alpha}(n_{\alpha}) = \hbar^{-1} \partial \omega_{\alpha}(n_{\alpha}) / \partial n_{\alpha}$. As a simple model, we assume $\hbar^2 |\omega'_{\alpha}| \ll \hbar \omega_{\alpha}$, and ω_{α} random with a small

but nonvanishing dispersion. The former restricts the role nonlinearities have in the local level densities, while the latter constrains all oscillators to have similar frequencies, and primarily affects the superexchange mechanism. H is thus represented by an ensemble of random matrices, with oscillator frequencies, nonlinearities, and coupling terms all chosen from probability distributions satisfying the constraints. We determine critical values of ϕ_3 and σ for energy to flow, revealing the central role of high-order resonances to ergodicity; regimes where energy flow occurs primarily via vibrational superexchange are also identified.

The approach we adopt generalizes one used by LW [4], who studied a many-dimensional low-order Fermi resonant system under different initial conditions where each oscillator is excited to moderate energies, drawing analogies between their model and the theory of Anderson localization in many dimensions. Their detailed analysis based on a probabilistic self-consistent theory is most directly related to the Anderson problem on a Cayley tree [13], where only direct low-order resonant couplings among zero-order states of a tight-binding Hamiltonian are considered. It has been shown that the complete probabilistic analysis is equivalent for the Anderson problem on the Cayley tree, to other field theoretic approaches based on the supersymmetric nonlinear σ model [14]. In our system, however, transitions often occur via off-resonant states at low energy, so that a Cayley tree topology is not immediately apparent. Moreover, at low energies the action space is no longer statistically homogeneous, so other simplifications used by LW must be removed. This lack of statistical homogeneity reflects the polyad structure of these nonlinear models, which has been studied extensively by molecular spectroscopists [15].

Information about whether an eigenstate overlapping site $|j\rangle$ with energy E is localized or extended is contained in the solution to the renormalized Feenberg perturbation series for the site self-energy [9,13]

$$S_j(E) = \sum_{k(\neq j)} V_{jk} [E - \epsilon_k - S_k^{(j)}(E)]^{-1} V_{kj} \\ + \sum_{k \neq j} \sum_{l \neq k, j} V_{jl} [E - \epsilon_l - S_l^{(jk)}(E)]^{-1} V_{lk} \\ \times [E - \epsilon_k - S_k^{(j)}(E)]^{-1} V_{kj} + \dots, \quad (2)$$

where each order M of S is

$$S_{j,M}(E) = \sum_{k,l,\dots,q} V_{jk} e_k^{-1} V_{kl} e_l^{-1} V_{lm} \dots e_q^{-1} V_{qj}. \quad (3)$$

The sums are restricted to nonrepeating paths, i.e., $k \neq j, l \neq k, j$, etc.; and $e_m = E - \epsilon_m - S_m^{(jkl)}(E)$, where (jkl) of $S_m(E)$ denotes that these sites are removed from its summation. In the analysis of $S_j(E)$ on a Cayley tree, only the first sum in (2) is retained, and an additional assumption introduced whereby expressions for $S_j(E)$ are conflated, i.e., $S_j \equiv S_j^{(k)} \equiv S_j^{(kl)}$, etc. For

our model, however, (2) cannot be truncated before at least the lowest-order terms coupling the initial state to states resonant to it. It is also apparent that a probability distribution for $S_j(E)$ of an initial state, say, $|m000\dots\rangle$, may be very different from that of most isoenergetic states. The latter typically has n excited modes, each with only a few quanta, $q \sim 1$. Because of nonlinearities, the rate of excitation transfer out of the initial state generally differs from that of transfer out of most other states. To differentiate them, we refer to the initial state, with all excitation in any one mode, as an edge state; and to the vast majority of states close in energy and having at most q quanta in any mode as interior states. Figure 1 illustrates distinctions between flow among interior states and flow from an edge state to the interior.

The energy and site self-energy are separated into their real and imaginary parts

$$E = \tilde{E} + i\eta, \quad S_j(E) = E_j(E) + i\Delta_j(E), \quad (4)$$

where the imposed external dephasing η is taken to be very small. Assume initially that all states are localized at energy E , thus $\Delta_j(E) \propto \eta$. $E_j(E)$ and $\Delta_j(E)$ then read [16]

$$E_j = \sum_{M=2}^{\infty} E_{j,M}, \quad \Delta_j = \sum_{M=2}^{\infty} \Delta_{j,M}, \quad (5a)$$

$$E_{j,M} = \sum_{k,l,\dots,q} V_{jk} X_k \dots X_q V_{qj}, \\ \Delta_{j,M} = \sum_{k,l,\dots,q} V_{jk} \dots V_{qj} \left[\sum_{\alpha=k}^q \prod_{\beta=k(\neq\alpha)}^q X_{\beta} Y_{\alpha} \right], \quad (5b)$$

$$X_j = [\tilde{E} - \epsilon_j - E_j]^{-1},$$

$$Y_j = [\tilde{E} - \epsilon_j - E_j]^{-2} (\eta + \Delta_j). \quad (5c)$$

In the limit $\mu_j \equiv \eta + \Delta_j \rightarrow \infty$, the M th-order terms are

$$E_{j,M} = \sum_{k,l,\dots,q} V_{jk} \dots V_{qj} \left[\sum_{\alpha=k}^q X_{\alpha}^{-1} \mu_{\alpha}^{-2} \prod_{\beta=k(\neq\alpha)}^q \mu_{\beta}^{-1} \right], \\ \Delta_{j,M} = \sum_{k,l,\dots,q} V_{jk} \dots V_{qj} \prod_{\alpha=k}^q \mu_{\alpha}^{-1}. \quad (6)$$

We determine criteria for flow among interior states, then treat the problem of flow out of an edge state. For interior states we may assume the probability distribution of $S_j(E)$ is the same for all sites; whether a state is localized or not can be determined using (5) and invoking self-consistency for the joint probability distribution $F(E_j, \Delta_j; \epsilon_j)$ with $\eta \rightarrow 0$ when states are localized. Self-consistency can be alternatively demanded from both localized and extended sides of the transition, which has the merit of yielding finite-value solutions to $\Delta(E; \epsilon_j)$ as well as incorporating dephasing effects expressed in terms of finite values of η . Mathematical treatment of

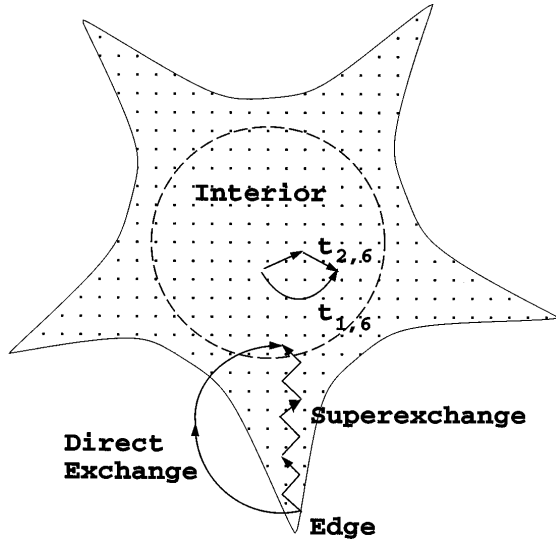


FIG. 1. Illustration of energy flow in the state space of the anharmonic oscillator Hamiltonian. Commencing from a vertex energy flows via numerous virtual transitions and direct couplings due to high-order resonances, to more and more states toward the interior. Direct and virtual transitions contribute to flow in the interior as indicated.

both localized and extended regimes is made tractable, as detailed in Ref. [4], by demanding a weaker self-consistency in which the most probable value of $\Delta(E; \epsilon_j)$ only is self-consistently determined. This is done by substituting $\Delta_{mp}(E; \epsilon_j)$ into Y_j of Eq. (5) and into μ_α of Eq. (6), defining $\mu(E; \epsilon_j) \equiv \eta + \Delta_{mp}(E; \epsilon_j)$. Thus in the limit $\mu \rightarrow 0$, the most probable value of Δ must lie at $\Delta = \Delta_{mp} \rightarrow 0$, whereby $|j\rangle$ is localized. Considering first the $\mu \rightarrow 0$ limit, we write the probability distribution for $\Delta(E; \epsilon_j)$, $f(\Delta; \epsilon_j)$, using (5) and (6) to fourth order. A

solution to $f(\Delta; \epsilon_j)$ is obtained by Fourier transforming, averaging over the disorder, then back transforming [4]. To make this procedure tractable, we substitute X_j of Eq. (5) with its average, $\langle X_j \rangle$, interpreted to be the typical inverse level spacing between the initial state and off-resonant levels directly coupled to it. This approach has been successfully applied in determining effects of band structure on transport in disordered solid state systems [16]. We finally obtain for $\Delta_{mp}^{(\text{int})}(E; \epsilon_j)$ in the limit $\mu \rightarrow 0$,

$$\begin{aligned} \Delta_{mp}^{(\text{int})}(E; \epsilon_j) &= T^{(\text{int})}(E; \epsilon_j) \mu(E; \epsilon_j) \\ &= \left[\sum_{\kappa, Q} t_{\kappa, Q}(E; \epsilon_j) \right]^2 \mu(E; \epsilon_j), \end{aligned} \quad (7)$$

where κ denotes order of perturbation and Q is the total quantum number change in a transition. Retaining the two lowest-order terms, and lowest order in V for each,

$$t_{1, Q}(E; \epsilon_j) = K_Q \langle |V_Q| \rangle D_R(E; \epsilon_j), \quad (8a)$$

$$t_{2, Q}(E; \epsilon_j) = \sum_l K_{l, Q} \langle |V_{Q/2}| \rangle^2 \langle X_l \rangle D_R(E; \epsilon_j); \quad (8b)$$

K_Q is the number of resonant states a distance Q in quantum number space from the initial state; $K_{l, Q}$ is the connectivity to resonant states via off-resonant states a distance l from the initial state; $V_k = \phi_3 \sigma^{3-k}$; $D_R(E; \epsilon_j)$ is the density of levels coupled resonantly to $|j\rangle$, and is assumed to be a Lorentzian whose width reflects the dispersion of ω_α .

In the limit $\mu \rightarrow 0$, Δ_{mp} is again found by demanding self-consistency. An adequate interpolation for Δ_{mp} between the limits of $\mu \rightarrow 0$ and $\mu \rightarrow \infty$ is made by substituting for $T^{(\text{int})}(E; \epsilon_j)$ the simple Padé approximant [4]

$$\Delta_{mp}^{(\text{int})}(E; \epsilon_j) = T^{(\text{int})}(E; \epsilon_j) \left[1 + \frac{T^{(\text{int})}(E; \epsilon_j)}{\sum_Q K_Q^{1/2} \langle |V_Q| \rangle} \mu^2(E; \epsilon_j) \right]^{-1} \mu(E; \epsilon_j). \quad (9)$$

Whether a state is localized or extended depends on whether $\Delta_{mp}^{(\text{int})}(E; \epsilon_j)$ is 0 or finite in the limit $\eta \rightarrow 0$. It is apparent that the only solution for Δ_{mp} when $T^{(\text{int})}(E; \epsilon_j) < 1$ is 0, whereas a finite value for Δ_{mp} and thus ergodic flow among interior states obtains when the sum is greater than the transition value of 1. Finite values of $\Delta_{mp}^{(\text{int})}$ in the extended regime, $T^{(\text{int})}(E; \epsilon_j) > 1$, can be estimated using Eq. (9).

We turn finally to the initial condition of one oscillator of H_0 excited to $m = N^\gamma$ quanta, $0 < \gamma < 1$, with the others in their ground state. One state among the nearest set of states resonant to the initial one has n_1 previously unexcited oscillators excited to q quanta; one among the next tier has n_2 oscillators excited, and so on. Proceeding as above, we express $\Delta_{mp}^{(\text{edge})}(E; \epsilon_j)$ in terms of its coupling to both interior and other edge states. The former are seen to dominate the rate, so that combining

orders of $\Delta(E; \epsilon_j)$ and σ we find for $\Delta_{mp}^{(\text{edge})}$ as $\eta \rightarrow 0$ the relation

$$\begin{aligned} \Delta_{mp}^{(\text{edge})}(E; \epsilon_j) &= T(E; \epsilon_j) \Delta_{mp}^{(\text{int})}(E; \epsilon_j) \\ &= \left[\sum_{\kappa, l} t_{\kappa, l}(E; \epsilon_j) \right]^2 \Delta_{mp}^{(\text{int})}(E; \epsilon_j), \end{aligned} \quad (10a)$$

$$t_{\kappa, l}(E; \epsilon_j) = \sum_m K_{m, l} \langle \tilde{V}_{2n_l/\kappa} \rangle^\kappa \left[\frac{\langle X_m \rangle}{D_R(E; \epsilon_j)} \right]^{\kappa-1}; \quad (10b)$$

$K_{m, l}$ is the connectivity to the l th set of resonant states, $l = 1$ being the set closest in quantum number space to the edge, via off-resonant states a distance m from the edge state; $\tilde{V}_k = V_k D_R(E; \epsilon_j)$. The criterion for energy to flow from the edge state to isoenergetic states thus amounts to whether or not the interior states are

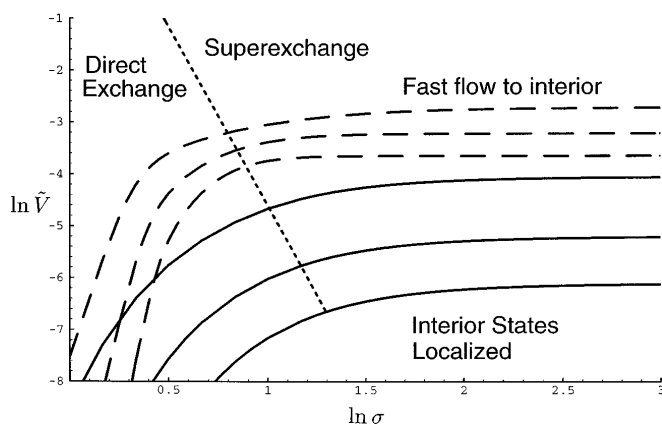


FIG. 2. Solid lines are critical values of $\tilde{V} = \phi_3 D_R(E; \epsilon)$ separating localized from extended states as a function of σ , for the model with $\gamma = 0.35$, $\delta = 0.70$. From top to bottom, $N = 54, 100, \text{ and } 166$. Dashed curves indicate crossover from slow to fast flow from an edge state to the interior. Short dashes separate the region where flow out of the initial state occurs via vibrational superexchange from that where direct coupling dominates.

extended. If they are extended, then flow throughout the state space at energy E is permitted. Crispness of the transition to global flow depends on whether $\rho_l(E) < \rho_g(E)$, enforced when $Z = N^\delta$ and $\delta < 1$. When $\delta = 1$, the transition may not be sharp but rather a crossover to direct global flow, a situation resembling cases containing single bottlenecks to flow [8].

Results for our model are summarized in Fig. 2, where critical values of the cubic coupling ϕ_3 separating localized from extended states are plotted against σ , the rate of exponential decrease in magnitude of higher-order coupling terms, for different numbers of oscillators listed below the figure. Also shown are regions of fast [$T(E; \epsilon_j) > 1$] and slow [$T(E; \epsilon_j) < 1$] energy flow to interior states. Figure 2 illustrates the relevance of higher-order resonances to the transition as N gets large. Low-order terms suffice to determine the transition to global flow only when $\sigma > N^\delta$. In Fig. 2 this is seen as the larger values of σ required to approach saturation in the transition curves as N increases. Physical values for σ often range between 3 and 10 [12], pointing up the importance of high-order resonances to energy flow for the systems plotted in Fig. 2. Generally in the thermodynamic limit high-order resonances are responsible for achieving ergodicity.

We have hereby established criteria and rates for ergodic flow among energetically accessible states of a many-dimensional oscillator system at energies near its ground state. We have examined the contributions of high-order resonances to global flow, which is found to occur above a transition threshold. We believe this energy

flow to be intimately related to the dynamical tunneling mechanism conjectured by Heller and Davis [10], though in some respects our approach does not completely address their conjecture. To do so would require determining rates for tunneling not between the unperturbed tori discussed here, but among the exact Kolmogorov-Arnold-Moser tori in many dimensions. Our understanding of many-dimensional quantum energy flow would greatly benefit from numerical studies, which have proven invaluable towards elucidating quantum ergodic properties of low-dimensional systems [1]. Computational studies of specific molecules at low energy [11,12] as well as an investigation [5] simulating energy flow in a random nonlinear oscillator system implicate an energy flow mechanism analogous to the one here.

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